

EXHIBIT S

Handbook of Material Weathering

4th Edition

George Wypych



ChemTec PUBLISHING

Toronto 2008

Published by ChemTec Publishing
38 Earswick Drive, Toronto, Ontario M1E 1C6, Canada

© ChemTec Publishing, 2008
ISBN 978-1-895198-38-6

Cover design: Anita Wypych

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Library and Archives Canada Cataloguing in Publication

Wypych, George

Handbook of material weathering/George Wypych.--4th ed.

First ed. published in 1990 as: Weathering handbook / Jerzy Wypych

Includes bibliographical references and index.

ISBN 978-1-895198-38-6

1. Materials--Deterioration--Handbooks, manuals, etc. 2. Materials--Biodeterioration--Handbooks, manuals, etc. 3. Polymers--Deterioration.
4. Polymers--Biodegradation. I. Wypych, George. Weathering Handbook. II. Title.

TA418.74.W96 2007

620.1'1223

C2007-904685-1

Printed in United States and United Kingdom

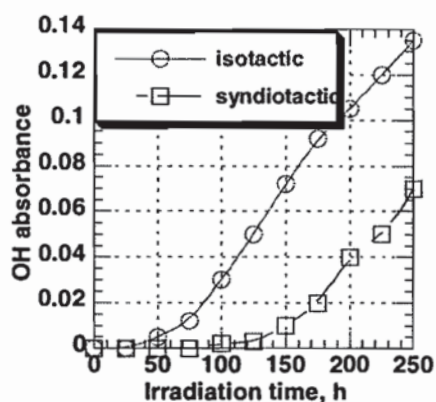


Figure 14.106. Hydroxyl group formation in iso- and syndiotactic polypropylenes irradiated with mercury lamp through Pyrex filter. [Data from Kato, M; Tsuruta, A; Kuroda, S; Osawa, Z, *Polym. Deg. Stab.*, 67, No.1, 2000, 1-5.]

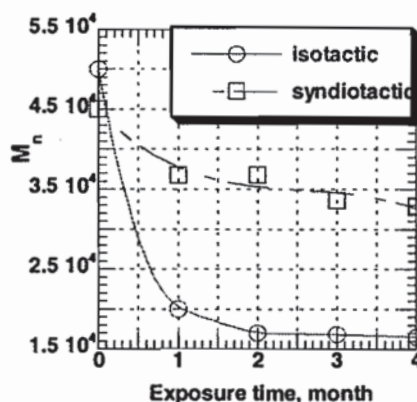


Figure 14.107. Number average molecular weight of iso- and syndiotactic polypropylenes vs. irradiation time with mercury lamp through Pyrex filter. [Data from Kato, M; Tsuruta, A; Kuroda, S; Osawa, Z, *Polym. Deg. Stab.*, 67, No.1, 2000, 1-5.]

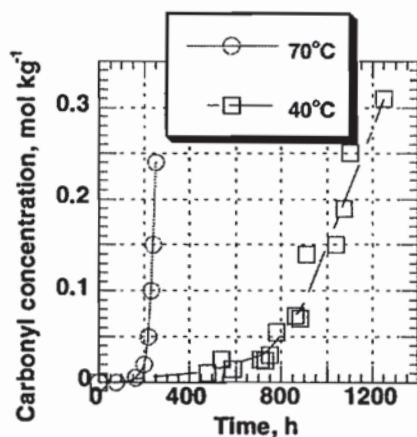


Figure 14.108. Effect of temperature on carbonyl group concentration in polypropylene exposed to fluorescent lamp radiation in the range of 300-500 nm. [Data from Audouin, L; Girois, S; Achimsky, L; Verdu, J, *Polym. Deg. Stab.*, 60, 1, 137-43, 1998.]

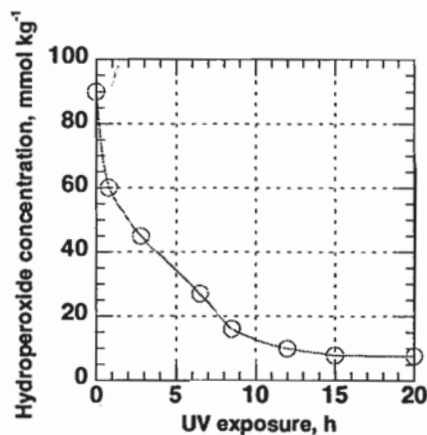


Figure 14.109. Hydroperoxide loss upon photolysis of preoxidized polypropylene exposed in SEPAP12-24 at 60°C. [Adapted, by permission, from Commercuc, S; Vaillant, D; Phillippart, JL; Lacoste, J; Lemaire, J; Carlsson, DJ, *Polym. Deg. Stab.*, 57, No.2, 1997, 175-82.]

14.26.3 CHARACTERISTIC CHANGES AND PROPERTIES

Raising the temperature of oxidation speeds up both the formation rate and the decomposition rate of hydroperoxides (Figure 14.100). When carbonyl concentration is high, the

$$y = -0.18286 + 0.082571x \quad R = 0.97563$$

$$y = 0.029366 + 0.0064141x \quad R = 0.99822$$

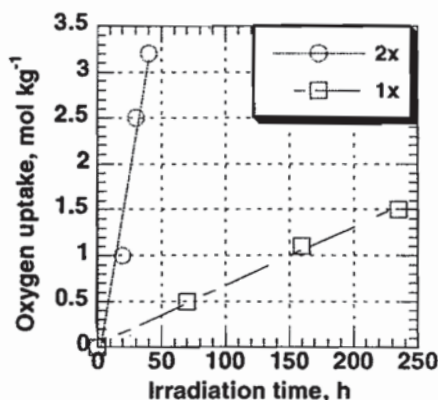


Figure 14.110. Oxygen uptake by samples of polypropylene exposed in SEPAP 12-24 equipped with two (1x) and four (2x) lamps. [Data from Phillippart, JL; Sinturel, C; Arnaud, R; Gardette, JL, *Polym. Deg. Stab.*, 64, 2, 213-25, 1999.]

$$y = 3.0946 + 0.019718x \quad R = 0.99701$$

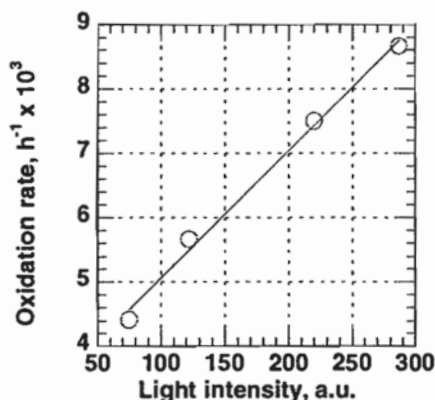


Figure 14.111. Effect of light intensity on oxidation rate of polypropylene exposed in SEPAP 12-24. [Data from Phillippart, JL; Sinturel, C; Gardette, JL, *Polym. Deg. Stab.*, 58, 3, 261-8, 1997.]

rate of formation of hydroperoxides is dependent on the rate of the initial thermooxidative processes (Figure 14.101). The kinetics and mechanisms of both thermal oxidation and photodegradation are interrelated (Figure 14.102). A significant difference between the usual photodegradation reaction routes in polypropylene and polyethylene lies in the accumulation of functional groups (Figure 14.103). As a result of photodegradation, more ester groups are formed and an aldehyde group is also generated.

Polypropylene has high oxygen uptake (higher than polyamide, poly(butylene terephthalate), and polyethylene, in this respective sequence) (Figure 14.104). Oxygen uptake is a linear function of time of exposure in Suntest.

The polypropylene structure influences its photooxidation rate (Figure 105).⁵⁸⁴ Hydroxyl groups are produced faster in isotactic than in syndiotactic polypropylene (Figure 14.106). The molecular weight of isotactic polypropylene is reduced rapidly whereas the molecular weight of syndiotactic polypropylene is not much affected (Figure 14.107).

The temperature of exposure has profound effect on carbonyl group formation (Figure 14.108).⁵⁹⁴ The combination of UV energy and thermal energy results in much higher degradation rates than encountered in the thermooxidation process. 90% of the hydroperoxide is decomposed on a brief exposure to UV radiation at 60°C (Figure 14.109). To obtain similar rate without UV radiation to the observed in Figure 14.109 the temperature had to be increased to 90°C.

Figure 14.110 shows that when radiation energy is doubled (four lamps (2x) used in SEPAP unit in place of two lamps (1x)) the oxygen uptake increases approximately 12 times. This indicates that oxygen uptake is not a linear function of irradiance. Oxidation

426

Data on Specific Polymers

$$y = 181.25 - 0.48294x \quad R = 0.98587$$

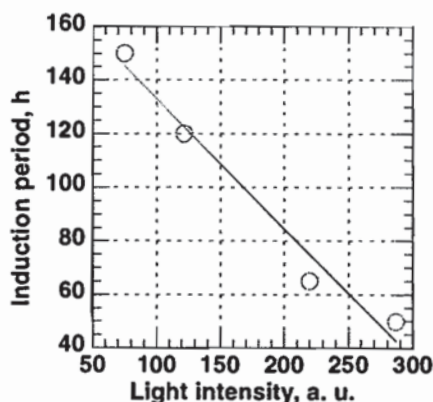


Figure 14.112. Effect of light intensity on induction period of propylene exposed in SEPAP 12-24. [Data from Phillipart, JL; Sinturel, C; Gardette, JL, *Polym. Deg. Stab.*, 58, 3, 261-8, 1997.]

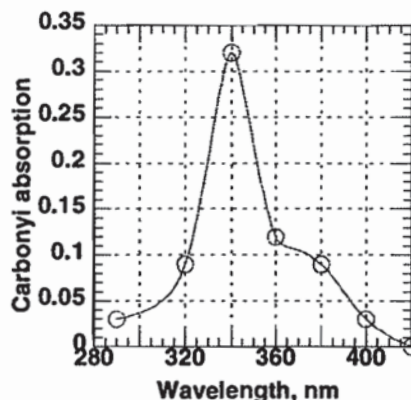


Figure 14.113. Activation spectrum of polypropylene film exposed with cut-off filters in Weather-Ometer for 119 h. [Data from Zhenfeng, Z; Xingzhou, H; Zubo, L, *Polym. Deg. Stab.*, 51, 93, 1996.]

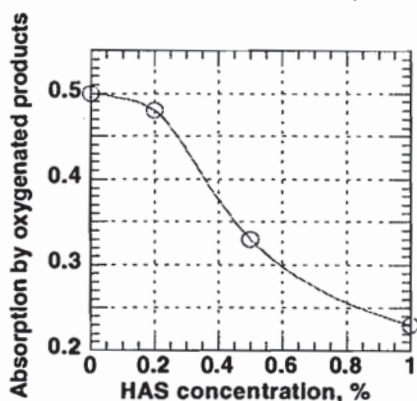


Figure 14.114. Effect of HAS concentration on formation of oxygenated products by polypropylene containing decabromodiphenylether as flame retardant. Samples exposed in SEPAP 12-24. [Data from Gardette, JL; Sinturel, C; Lemaire, J, *Polym. Deg. Stab.*, 64, 3, 411-7, 1999.]

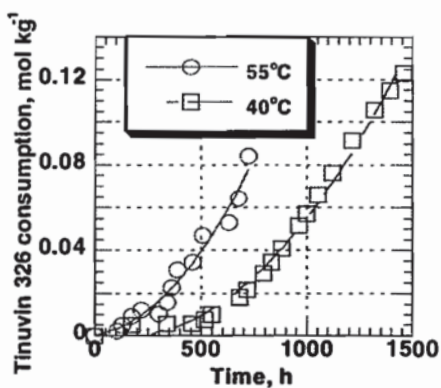


Figure 14.115. Photochemical consumption of Tinuvin 326, having initial concentration of $1.58 \times 10^{-3} \text{ mol kg}^{-1}$, in 100 μm polypropylene film exposed to radiation of 300 to 450 nm at different temperatures. [Data from Girois, S; Delprat, P; Audouin, P; Verdu, J, *Polym. Deg. Stab.*, 64, 1, 107-14, 1999.]

rate increases linearly as the light intensity increases (Figure 14.111) whereas induction period is inversely proportional to light intensity (Figure 14.112).

Figure 14.113 shows the activation spectrum of polypropylene measured by rate of carbonyl group formation.⁶³⁶ Radiation around 330 nm degrades polypropylene most effectively.

Flame retardants are known to affect the thermal and photolytic stability of polypropylene. Figure 14.114 shows that smaller addition of stabilizer (0.2%) almost does not affect oxidation process. Temperature has very strong influence on the rate of consumption of UV absorber (Figure 14.115). A temperature increase of 15°C increases UV absorber consumption four times. Filler (talc/calcium carbonate) addition reduced weather stability but surface treatment of filler helped to retain properties.⁶⁸²

Tensile strength and strain values change linearly with carbonyl index concentration.⁶⁷⁴ Carbonyl index determined by FTIR is thus a very good indicator of the weathering progress.^{674,675} Density and crystallinity of PP increase with degradation time and the radiation energy delivered to the samples.^{678,685} Molecular weight of PP decreases on exposure to UV radiation due to the chain scissions in surface layers.⁶⁸¹ Polymorphic transformation from β - to α -crystallites occurs during exposure to UV radiation.^{681,687}

PP photooxidation can be divided into four well-defined periods:⁶⁸⁸

- incubation period (first 3-5 days) – effects of photochemical reaction are not visible (absence of cracks and changes in mechanical properties)
- surface cracking (5 to 20 days) – surface embrittlement and drop in Young's modulus because of formation of cracks
- chemicrystallization on surface (3 to 5 weeks) – chain scissions in amorphous phase, segment migration, chemicrystallization, formation of small (unattached) crystallites which do not improve mechanical properties (mechanical properties actually deteriorate because of numerous cracks on the surface)
- stabilization (5 to 7 weeks) – no further formation of cracks, surface photooxidized, and core protected by surface changes.

14.26.4 DATA

Luminescence data:		
Sample form	Excitation wavelength, nm	Emission wavelength, nm
film	230, 285	309, 320
film	270, 290, 330	420, 445, 480, 510
film (thermally degraded)	330	430, 480, 520
film (thermally degraded)	230	295, 330, 400
film (thermally degraded)	287	320-330, 470
film (thermally degraded)	230, 290	340
film (thermally degraded)	230, 283	340
film (thermally degraded)	323	332
film (thermally degraded)	295	342
atactic PP	232	330
	290	340
Activation wavelength: 310 nm		Spectral sensitivity: 320-360; 300-350
Products of photolysis: free radicals, crosslinks		
Products of photooxidation: free radicals, hydroperoxides, carbonyl groups, chain scissions		
Important initiators and accelerators: all listed for PE and titanium polymerization catalyst		